Main-Chain Functionalization of Poly(L-lactide) with Pendant Unsaturations

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ABSTRACT: Main-chain-functionalized poly(L-lactide) (PLLA) with pendant unsaturations was synthesized through a one-pot postpolymerization procedure with the PLLA homopolymer as the starting material. The material was functionalized through α -hydrogen abstraction by a sterically hindered strong base, lithium diisopropylamide, followed by the addition of an acid chloride. Two different acid chlorides were examined, lauroyl chloride as a concept electrophile and oleoyl chloride to provide the pendant unsaturations. The semisolvated system, together with

branching reactions from the alpha position of the acid chloride, yielded a high molar amount of the incorporated reactant in the material. The unsaturations were preserved under the chosen conditions and the material exhibited surfactant-like properties in blends with oleic acid and PLLA. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: branched; graft copolymer; LDA; polyester; postpolymerization modification

INTRODUCTION A key step in designing new functional polymers is the choice of raw material, as this will govern the material's inherent properties such as degradation characteristics, mechanical properties, and hydrophilicity. The basic chemical structure of the polymer will also regulate the possibility of postpolymerization alterations that permit a tailoring of its inherent properties toward a specific application. Poly(L-lactide) (PLLA) can be polymerized from renewable resources, and it is expected to be an alternative to many of the petroleum-based materials in the near future, although some properties need to be improved in order for it to be an equal match.

One major drawback of PLLA is it nonfunctionality, that is, in its pure form, it lacks easily accessible and easily transformable sites in the main chain that are susceptible to chemical alteration. Various strategies for achieving a functional PLLA have therefore been developed, such as ring-opening copolymerization with a functional monomer,^{1–6} the use of a functional initiator,^{7–10} and various post polymerization modifications.^{7,11–13}

A crucial aspect to consider when copolymerizing L-lactide with a functional lactone is that the functionality must be retained during polymerization, and that, for example, the monomer is sufficiently ring-strained to enable ring-opening polymerization. Over the years, many lactones bearing different functional groups have been successfully polymerized by ring-opening polymerization in a controlled way together with L-lactide or as pure homopolymers, with functionalities including alkynes,^{4,6,14} alkenes,^{1,2,5} ethers,^{15,16} ketones,¹⁷ epoxides,³ and so forth. These functional polymers make it possible to steer the properties of PLLA toward a specific application. However, the synthetic pathway in terms of raw material, number of reaction steps and yield, together with the reagents and solvents necessary for obtaining the functional monomer/polymer are of immense importance for achieving a wider commercial significance.

Another approach to form a functional PLLA is to use a functional initiator in the ring-opening polymerization. This initiator can either be molecular^{7,9,10} or macromolecular.⁸ Our group has developed a functional macroinitiator based on the condensation reaction between malonic acid and 2butene-1,4-diol, which gives a PLLA material with superior mechanical properties, in terms of elongation at break, and a more rapid degradation profile compared to that of PLLA homopolymer.^{8,18}

Postpolymerization modification offers a convenient and easy way to introduce functionality into PLLA. Two synthetic strategies are generally utilized for postpolymerization modification, either an end-group modification¹⁹ or a reaction on the polymer backbone.^{12,13} The postpolymerization modification of the polymer backbone opens the possibility of a greater degree of alteration simply due to the greater abundance of reaction sites. The most active site in the PLLA repeating unit, besides the ester moiety, is the slightly acidic

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SCHEME 1 The different reaction pathways that arise from the duality of the reactant lauroyl chloride (LOC). [S₁] is believed to be the major reaction for the covalent attachment of lauroyl chloride to PLLA main chain and [S₂], and [S₃] are the major branching and end-group reactions.

 α -proton. The α -proton of PLLA can be abstracted using a sterically hindered strong base to form a macroanion. The major problem is that the ester groups are susceptible to nucleophilic attack originating from the formed polyanion and this in turn fragments the polymer chain.^{12,13} A surface-assisted modification procedure can to a certain extent reduce high bulk degradation but does not change the polymers bulk properties.²⁰

The aim of this work was to synthesize a main-chain-functionalized PLLA-based material with pendant functionality. The approach adopted was an α -hydrogen abstraction from the L-lactide repeating unit, followed by the addition of an electrophile with a pendant unsaturation. We hypothesize that by using a semisolvated system together with an electrophile that can offer both monoaddition and different branching reactions, a material with a high degree of functionality should be obtainable.

RESULTS AND DISCUSSION

Ester structures with accessible α -protons offer the possibility for direct α -alkylation with an electrophile through anionic activation. This synthetic methodology has been used both in the monomeric stage and in postpolymerization modifications of aliphatic polyesters.^{12,13,21} The postpolymerization modification through anionic activation of PLLA can roughly be divided into two different approaches, as either bulk or surface modification. The bulk or surface modification is controlled by choosing a solvent or a nonsolvent for the polymer as the reaction medium. The general procedure for both approaches is as follows a non-nucleophilic strong base, that is, lithium diisopropylamide (LDA) abstracts the α proton of the ester moiety, forming a polymeric macroanion. After the polymeric anion is formed, the electrophile is added and terminates the reaction, Scheme $1.^{12,13,20}\ \mbox{The}$ major drawback of this reaction is that it strongly fragments

the polymer chain, mainly through back-biting reactions originating from the macroanion. From this point of view, the surface modification procedure is more favorable because the bulk is shielded from degradation; on the other hand, it also yields an inhomogeneous material. In light of this, our synthetic procedure is based on a semisolvated system to combine the advantages of the two methods.

PLLAs solubility in toluene is very temperature dependent and this makes it possible to create a system where the solubility of PLLA can be altered during the reaction. PLLA was therefore dissolved in toluene at 100 °C, followed by a rapid decrease in temperature to -78 °C. As the polymer started to precipitate, the LDA was added. The reaction mixture was subsequently stirred for 5 min and then terminated by the addition of the electrophile. To form a PLLA-based material with a pendant functionalizable site in the main chain, two fatty acid chlorides were chosen, lauroyl chloride (LOC) and oleoyl chloride (OOC). LOC was used as a concept electrophile to access the system and to eliminate reactions originating from the unsaturation of OOC.

Synthesis and Characterization of Poly(L-lactide-g-lauroyl)

LOC was used as a concept electrophile for the covalent attachment of a fatty acid structure to the main chain of PLLA. The covalent attachment of lauroyl (LO) to the main chain can be seen in ¹H nuclear magnetic resonance (NMR) as a change in the chemical shift corresponding to the α -protons in LOC, and poly(L-lactide-*g*-lauroyl) (PLLA-*g*-LO), as shown in, Figure 1. The α -protons have a very distinctive triplet originating from its two equivalent neighboring protons, PLLA-*g*-LO and LOC α -protons have a chemical shift of δ 2.33 ppm and δ 2.87 ppm, respectively, Figure 2. The ¹H NMR spectra also revealed a reduction in the relative amount of α -protons (δ 2.33 ppm) in relation to the Ω -protons (δ 0.90 ppm) in the material, which is a consequence of branching reactions originating from the reactive duality of LOC. Under the reaction, the polymer is subjected to highly



FIGURE 1 ¹H NMR of the product mixture obtained from the reaction with peak-designation according to the major product [S₁].



FIGURE 2 The displacement of the chemical shift for lauroyl chloride (LOC) α -protons as a result of the reaction with anionically activated PLLA to give the product PLLA-*g*-LO.

basic conditions. This result in that some sites on the polymeric backbone can remain anionically activated under the precipitation step with MeOH and as a consequence gives rise to the depicted acid base reactions in Scheme 2.

There are three dominating reaction pathways between LDA, PLLA, and LOC, occurring simultaneously, that lead to the incorporation of lauoryl (LO) and oleoyl (OO)-structures in the material. These pathways are shown in Scheme 1 where $[S_1]$ is believed to be the most probable and dominating path. In addition to $[S_1]$, other reactions such as further branching, $[S_2]$, and end-group reactions, $[S_3]$, can also occur. The proportion of LO incorporated into the material is almost linearly dependent on the increasing proportion of LDA to PLLA, Figure 3. However, a higher proportion of LDA to PLLA in the reaction simultaneously leads to more fragmentation, Figure 4.

Size exclusion chromatography (SEC) revealed the formation of three separate fractions, Figure 4, and a bulk decrease in M_n with increasing ratio of LDA and acid chloride to PLLA. However, the highest molecular weight fraction had a slight increase in molecular weight with increasing LDA and LOC in the reaction. This increase in molecular weight is believed to originate from the small precipitated assemblies of PLLA with LO-structures attached on the surface, stemming from reactions [S₁] and [S₂], Scheme 1. The hydrodynamic volume of a polymer chain is greatly influenced by an inherent solubility of its component. The difference in solubility of the grafted components makes it difficult to draw definite con-



FIGURE 3 Proportion of fatty-structures in the material determined from ¹H NMR as a function of starting reaction equivalents of LDA to PLLA.

clusions regarding the degrees of attached fatty-structures to PLLA solely through changes in the molecular weight, Figure 4 and Table 1. The two other elution peaks originate from the fragmented polymer chains from the surface of the precipitate that to different degrees are functionalized by the acid chloride, stemming from a mixture of pathways $[S_1]$, $[S_2]$, and $[S_3]$, Scheme 1.

Synthesis of Poly(L-lactide-g-oleoyl)

Poly(L-lactide-g-OOLA) (PLLA-g-OO) was synthesized by attaching OOC to the PLLA main chain in same manner as for PLLA-g-LO, which confirmed that the same synthetic strategy could be applied to both electrophiles, and the ¹H NMR spectra showed that the unsaturation (δ 5.42 ppm) remained intact, Figure 5. The reaction was performed with a batch size 10 times greater than previously described, and the material had the same features regarding different elution peaks for the low molar proportion of LDA to PLLA but yielded a fully fragmented material with a larger molar proportion of LDA to PLLA, Figure 6 and Table 2. This effect is due to the larger batch size, for example, more reagent and longer addition time. This longer addition time meant that the precipitated structures of PLLA were fully consumed, that is, degraded, before termination with methanol.

The dual nature, in terms of miscibility for the functionalized PLLA, was studied by blending of PLLA-g-OO₁₅, PLLA and oleic acid (OA) in various compositions Table 3. The degradation behavior of PLLA is strongly influenced by its molecular weight and molecular weight distribution. The heterogeneity in molecular weight for PLLA-g-OO₁₅, together with the



SCHEME 2 Acid–base reactions between PLLA chain and methanol in the precipitation step.





FIGURE 4 SEC elution curves for PLLA-*g*-LO with different initial molar ratios of LDA and lauroyl chloride to PLLA.

carboxylic acid groups from OA, in the blends should further increase the degradation. This should mean that these blended materials would show a more rapid degradation profile in comparison to pure PLLA.

Blends with Poly(L-lactide-g-oleoyl)

The thermal properties of the blends, evaluated by differential scanning calorimetry (DSC), showed that the $T_{\rm g}$ for PLLA increased slightly in the blended material. The relative crystallinity, defined as the melting transition of the PLLA fraction in the blended material, also increased in all of the blends, Table 4. It is therefore concluded that the fatty acid phase in the material has an antiplasticizing ability on the PLLA phase. The fatty acid phase helps the PLLA phase to order itself into a more crystalline structure by being embedded in the amorphous phase and pushing the PLLA chains to a more crystalline order. Added PLLA-g-OO₁₅ in the blends resulted in an even higher relative crystallinity then in the two-component blends with only PLLA and OA, Table 4. The more crystalline features of the PLLA phase



FIGURE 5 ¹H NMR of the product mixture obtained from the reaction, with peak-designation for PLLA-g-OO as the major product [S₁].



FIGURE 6 SEC elution curves for PLLA-*g*-OO with different initial molar ratios of LDA and oleoyl chloride to PLLA.

also hinder the mobility of the amorphous phase, and the $T_{\rm g}$ therefore is increased.

The mechanical properties further support the antiplasticizing ability of OA in the different blends, Table 4. Only a small decrease in the E-modulus was found after further addition of PLLA-g-OO₁₅ and OA to the blends, Table 4. The strain-atbreak decreased rapidly with increasing amount PLLA-g-OO₁₅ in the blends, but the E-modulus seemed to be less affected in three-component blend than the pure PLLA and OA, Table 4. The smaller effect on the E-modulus in the blends with PLLA-g-OO₁₅ is in direct relation to the observed higher relative crystallinity in the blends, Table 4. This indicates that PLLA-g-OO₁₅ acts in some way as a surfactant encapsulating the OA and allowing the PLLA phase to organize into more crystalline clusters.

As the fraction of PLLA-*g*-OO₁₅ increased in relation to the weight fraction of OA, the relative molar melt enthalpy value $(\Delta H_{\rm f,OA})$ for OA decreased, see Table 4. The decrease in $\Delta H_{\rm f,OA}$ also confirms the surfactant-like properties of PLLA-*g*-OO₁₅ in the blends, because this property should hinder the melt transition of OA by the branched OO-structures protruding into the OA phase.

The scanning electron microscope (SEM) images confirm why there is a drastic decrease in strain-at-break for the blended material, Table 4. The visual information about the different blends revealed that they have very porous surfaces, in comparison to the pure PLLA sample that is completely smooth. A higher fraction of PLLA-*g*-OO₁₅ to OA yields a material with more homogeneously distributed and smaller pores, Figure 7, and this also explain the more maintained E-modulus. The porous structures in the material are believed to originate from the solvent-casting procedure and are an effect of the immiscible nature of the different components.^{22,23} In summary, the blending system can be described as a micellar system, where PLLA is the matrix, PLLA-*g*-OO₁₅ the surfactant and OA the micelles. The immiscible nature of the PLLA and OA make it is possible to tailor

TABLE 1	$M_{\rm n}$	Values	of the	Different	Elution	Peaks	Obtained by SEC	
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Polymer Name	n _(%LDA)	<i>M</i> _n Last Fraction (g/mol)	<i>M</i> _n Second Fraction (g/mol)	<i>M</i> _n First Fraction (g/mol)
PLLA	0	144,600	-	-
PLLA-g-LO ₄ ^a	12.5	151,600	16,400	2,200
PLLA-g-LO ₂₅ ^a	200	152,900	6,600	1,500

^a The number denotes the molar amount of oleoyl-structures in the polymer determined by ¹H NMR.

the size and amount of the porous features by using a predetermined ratio of surfactant (PLLA-g-OO₁₅) to OA.

EXPERIMENTAL

Materials

The reactants, LDA (1.8 M, Sigma-Aldrich), oxalyl chloride (99%, Sigma-Aldrich), LOC (98%, Sigma-Aldrich), and OA (90%, Alfa Aesar) and the solvents, toluene (99, 8%; Sigma-Aldrich), dichloromethane 99.5%; Sigma-Aldrich), hexane (general purpose grade, Fischer Scientific, Germany), and methanol (general purpose grade, Fischer Scientific, Germany) were used as received.

The catalysts, stannous 2-ethylhexanoate, $Sn(Oct)_2$ (Sigma-Aldrich), and the initiator ethylene glycol (Merck, Germany), were dried over molecular sieves and placed under an inert N_2 atmosphere before use. The monomer L-lactide (Serva Feinbiochemica) was recrystallized twice from toluene before use.

Synthesis of Oleoyl Chloride

OOC was synthesized by reacting OA with oxalyl chloride in dichloromethane. The general procedure was as follows: OA (57 mmol) was dissolved in a 250-mL two-headed round-bottomed flask in dichloromethane (200 mL) at 0 °C followed by the slow addition of oxalyl chloride (85.5 mmol) under an inert atmosphere. After 15 min, the mixture was placed in an oil bath at 40 °C, and the reaction was followed by ¹H NMR. The reaction was complete after 6 h. The product was concentrated in vacuum and used without further purification.

Polymerization of L-lactide

All glassware was silanized before use and stored under a N_2 atmosphere. The polymerization of L-lactide was performed in bulk at 110 °C for 72 h with Sn(Oct)₂ (1:10,000 monomer ratio) as a catalyst and ethylene glycol (1:600 monomer ratio) as initiator.²⁴ The polymer was precipitated three consecutive times in a 95:5 hexane/methanol mixture.

Synthesis of Poly(L-lactide-g-lauroyl) and Poly(L-lactide-g-oleoyl)

PLLA-*g*-LO and poly(L-lactide-*g*-oleoyl) (PLLA-*g*-OO) were synthesized through postpolymerization functionalization of PLLA. The different electrophiles, laroyl chloride (LOC) and OOC, were covalently bonded to PLLA main chain according to the procedure described below. All reaction glassware was silanized and dried at 110 °C over night before use. PLLA (3.55 and 35.5 mmol for the synthesis of PLLA-*g*-LO and PLLA-*g*-OO, respectively) was dissolved in dry toluene (0.2 M) at 100 °C followed by rapid cooling to -78 °C. On precipitation of PLLA, LDA was added. The solution was stirred for ~5 min followed by the addition of LOC or OOC (twice the equivalent of LDA). The mixtures were stirred at -78 °C and at ambient temperature for 30 min, respectively. The mixtures were concentrated and precipitated at -18 °C in pure methanol.

Solution Casting of Films

Neat and blended films were made by solution casting in a 10 % (w/w) mixture of PLLA, PLLA-*g*-OO, and OA in chloroform. The mixtures were dissolved in a vial and placed on a shaker (yellow line os, 10 basic) for 2 h. The solutions were then poured into Petri dishes and placed in a fume hood. The solutes were then allowed evaporate, leaving films with an approximate thickness of 150 μ m.

Characterization

Nuclear Magnetic Resonance Spectroscopy

¹H NMR spectra were recorded on a Bruker DMX-500 NMR spectrometer at 500 MHz and analyzed using Bruker software. Samples ~10 mg in weight were dissolved in CDCl₃ (Aldrich Chemical) in 5-mm external diameter sample tubes. Nondeuterated chloroform was used as an internal standard ($\delta = 7.26$ ppm). The total amounts of LO and OO structures (X_t) in the sample were determined by evaluation of the integral peaks given by $X_t = \frac{l_{\Omega opt}/3}{l_{PLLA} + l_{sopl}/2}$ using the mean of three independent ¹H NMR spectra. The Ω-protons are divided by the α-protons corresponding to the repeating unit and OO group.

TABLE 2 M_n Values of the Different Elution Peaks Obtained by SEC

Polymer Name	n _(%LDA)	<i>M</i> _n Fraction 1 (g/mol)	<i>M</i> _n Second Fraction (g/mol)	<i>M</i> _n First Fraction (g/mol)	Yield (%)
PLLA	0	118,000	-	-	95
PLLA-g-005 ^a	12.5	91,900	9,100	400	71
PLLA- <i>g</i> -00 ₁₅ ^a	100	-	12,600	-	37

^a The number denotes the molar amount of oleoyl-structures in the polymer determined by ¹H NMR.



Name (B(^x PLLA- <i>PLLA</i> -g- <i>OO₁₅-^x</i> OA))	PLLA (% w/w)	PLLA- <i>g</i> -OO ₁₅ (% w/w)	Oleic Acid (% w/w)	Total Amount of Fatty Acid (% w/w) [#]
PLLA	100	0	0	0
B(⁸⁰ PLLA- ¹⁵ <i>PLLA</i> -g- <i>OO</i> ⁵ ₁₅₋ OA)	80	15	5	8.0
B(⁸⁰ PLLA- ¹⁰ <i>PLLA</i> -g- <i>OO</i> ¹⁰ ₁₅₋ OA)	80	10	10	11.8
B(⁸⁰ PLLA- ⁵ <i>PLLA</i> -g- <i>OO</i> ₁₅ - ¹⁵ OA)	80	5	15	18.0
B(⁶⁰ PLLA- ²⁰ <i>PLLA</i> -g- <i>OO</i> ₁₅ - ²⁰ OA)	60	20	20	23.0
B(⁸⁰ PLLA- ²⁰ OA)	80	0	20	22.0

^aThe number denotes the molar amount of oleoyl-structures determined from ¹H NMR in the material.

Differential Scanning Calorimetry

The thermal properties of the materials were investigated using DSC (Mettler Toledo DSC 820 module) under a nitrogen atmosphere. About 2–10 mg of the polymer was incapsulated in a 40- μ L aluminum container without pin. The specimens where heated from –55 to 200 °C and then cooled to –55 °C and thereafter heated again to 200 °C at a rate of 10 °C/min. The $T_{\rm g}$ and $T_{\rm m}$ values were recorded after the first heating scan. $T_{\rm g}$ was determined as the midpoint temperature of the glass transition, and the $T_{\rm m}$ as the maximum value of the melting peak.

Size Exclusion Chromatography

SEC was used to monitor the changes in molecular weight and dispersity of the synthesized polymer before and after the functionalization. The polymers were analyzed with a Verotech PL-GPC 50 Plus system equipped with a PL-RI Detector and two PolarGel-M Organic ($300 \times 7.5 \text{ mm}^2$) columns from Varian. The samples were injected with a PL-AS RT Autosampler for PL-GPC 50 Plus, and tetrahydrofuran (THF) was used as mobile phase (1 mL/min, 35 °C). The system was calibrated using polystyrene standards. Corrections for flow rate fluctuations were made using toluene as an internal standard. CirrusTM gel permeation chromatography (GPC) Software was used to process the data.

Scanning Electron Microscope

The microstructure of the blends was evaluated on the produced films by means of a JOEL JSM-5400 SEM using an acceleration voltage of 10 kV. The samples were mounted on metal stubs and sputter-coated with gold and platinum (2 nm) using a Denton Vacuum Desk II cold sputter etch unit operating at 45 mA for 2 s. The films were placed in a vacuum oven for 24 h before analysis, and the samples were randomly chosen from a representative piece of the material.

^xDenotes the added %(w/w) composition in the blend.

CONCLUSIONS

We have successfully synthesized a highly functionalized PLLA-based material with pendant unsaturations by abstracting the α -hydrogen of the lactide repeating unit using the sterically hindered strong base, LDA, followed by the addition of an electrophile. A semisolvated system together with branching reactions originating from the electrophile yielded a high molar amount of reactant incorporated into the material. The amount of LOC incorporated into the material was controlled in the range of 2-63 mol % with increasing LDA in the reaction. Reaction with the unsaturated electrophile, OOC, at two different equivalents of LDA yielded 5 and 15 mol % of incorporated 00-structures in the material. ¹H NMR also revealed that the unsaturation remained intact under these reaction conditions, which is a vital for further functionalization. The properties of PLLA grafted with 15 mol % (PLLA-g-OO₁₅) were evaluated in blends solvent-cast together with OA and PLLA. The $T_{\rm g}$ increased slightly in all of the blends originating from the antiplasticizing ability of OA. The E-modulus was almost constant in the three-component blend between PLLA, OA, and PLLA-g-OO₁₅, even with

Name (B([×] PLLA- [×] <i>PLO15</i> - [×] OA))	ΔT_{g} (°C)	Relative Crystallinity (%)	E-Modulus (MPa)	Strain at Break (%)	$\Delta H_{\rm f.OA}^{a}$ (J/g)	$\Delta H_{\rm f.OA}$ / ^b $n_{\rm OA}$ ⁿ (J/mol.OA)
PLLA	0 ± 0.4	49 ± 2.4	11.7 ± 1.3	8.9 ± 3.1	-	_
B(⁸⁰ PLLA- ¹⁵ <i>PLO15</i> - ⁵ OA)	3.5 ± 0.8	58 ± 2.9	10.6 ± 0.9	5.4 ± 1.4	3.4 ± 0.1	41.8 ± 0.9
B(⁸⁰ PLLA- ¹⁰ <i>PLO15</i> - ¹⁰ OA)	2.6 ± 0.3	58 ± 2.2	9.5 ± 0.6	3.5 ± 1.3	8.1 ± 0.1	68.4 ± 4.0
B(⁸⁰ PLLA- ⁵ <i>PLO15</i> - ¹⁵ OA)	2.8 ± 0	64 ± 2	10.6 ± 0.4	5.4 ± 1.8	14.1 ± 0.2	61.5 ± 1.0
B(⁶⁰ PLLA- ²⁰ <i>PLO15</i> - ²⁰ OA)	3.6 ± 0.3	64 ± 1.4	8.8 ± 1.4	3.7 ± 1.0	15.1 ± 1.4	83.8 ± 8.1
B(⁸⁰ PLLA- ²⁰ OA)	2.9 ± 0.1	56 ± 0.8	6.5 ± 0.7	3.7 ± 0.9	23.7 ± 0.7	107.4 ± 3.0

TABLE 4 Thermal and Mechanical Properties of the Blends

^xThe added % (w/w) composition in the blend.

 $^{\rm a}$ The value of the peak corresponding to the melt transition of oleic acid at 7–16 $^\circ C$ obtained from DSC.

^b The molar amount of oleic acid in the material obtained from ¹H NMR. ^{*n*}The melting value for 1 mol of oleic acid (OA) in a blend with the particular composition of PLLA, PLLA-g-OO₁₅ and OA.





FIGURE 7 The dark areas represent the porous structures in the material with various compositions of PLLA, PLLA-g-OO₁₅ and OA in the blend.

high molar equivalents of OA and PLLA-g-OO₁₅, but the strain at break was greatly reduced. SEM images revealed a larger amount of small porous structures with increasing proportion of PLLA-g-OO₁₅ to OA in the material. It is proposed that the PLLA-g-OO₁₅ acts as a surfactant and disperses the OA phase in the PLLA matrix, resulting in more and smaller porous structures in the material blend.

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